Investigations on the ZnO- and Cr-doped ZnO powders

YONG-KEUN CHOI¹, KYEONG MIN KIM¹, YONGCHEOL JANG¹, HAKYUNG JEONG²,
VIJAY SINGH³ and SENTHIL KUMARAN RANGARAJULU^{1,*}

¹Department of Biological Engineering, Konkuk University, Seoul 05029, Korea

²Department of Mechanical Design and Production Engineering, Konkuk University, Seoul 05029, Korea

³Department of Chemical Engineering, Konkuk University, Seoul 05029, Korea

*Author for correspondence (kumaran.ran@gmail.com)

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Abstract. Among the metal–oxide nanoparticles, pure and doped zinc oxide (ZnO) has been widely studied due to their potential applications, such as electrical, thermal and optical materials. In this context, samples of undoped ZnO and Cr-doped ZnO powders were prepared using a solution-combustion route. The formation of the combustion products was confirmed by X-ray diffraction analysis. The samples were well characterized using the Fourier transform infrared spectroscopy and scanning electron microscopy techniques. In the sample, photoluminescence studies showed that ZnO could be excited at 267 nm, while an ultraviolet emission centred at ~383 nm was exhibited. Antibacterial-activity testing was carried out using the disc-diffusion method.

Keywords. ZnO; combustion synthesis; photoluminescence; antibacterial activity.

1. Introduction

Zinc oxide (ZnO) is a common additive with a variety of applications. Due to its wide bandgap of 3.37 eV and interesting magnetic, chemical, morphological and optical properties, synthetic ZnO has been studied widely during the past several years [1–5]. The synthetic version is attractive in many technological fields, such as solar cells [6], gas sensors [7], varistors [8] and short-wavelength optoelectronic devices [9]. The antimicrobial properties of ZnO powders have also been confirmed [10]. From the literature, it is clear that researchers have found that smaller ZnO-powder particles are more effective than the larger particles against both Gram-negative and Gram-positive bacteria [10–12]. A wealth of available literature-based information shows that the doping process improves the antibacterial activity of ZnO [13–15]; especially, dopants like those of magnesium (Mg), antimony (Sb), cobalt (Co), manganese (Mn) and selenium (Sn) play an important role in the enhancement of the antimicrobial activities of ZnO [15–17]. In this context, the preparation of both undoped ZnO and chromium (Cr)-doped ZnO was completed using a combustion process, and the antibacterial activities of these samples were subsequently investigated. The reported work in the literature suggests that the efficient antibacterial properties of the nanostructure of ZnO make it a possible candidate for the varieties of the following applications: medical and cloth coatings, water purification, bio-imaging and drug delivery, and food preservation and packaging systems [17–21].

The synthesis of ZnO has been achieved using a variety of routes, such as solid-state reactions [22], sol–gel processing [23], hydrothermal processing [24], spray pyrolysis

[25] and microemulsion precipitation [26]. All these methods, however, are tedious, time-consuming and require the use of expensive chemicals and instruments. In consideration of this information, and due to the great demand for an economically viable synthesis method, a combustion-synthesis method that is very advantageous due to benefits, such as a sound homogeneity owing to molecular-level mixing, energy saving, and a safe and easy operation was employed for the preparation of ZnO and Cr-doped ZnO in the present study. The prepared combustion product was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and photoluminescence (PL) techniques. Also, an investigation of the antibacterial activity of the prepared samples against the Gram-positive bacterium *Bacillus subtilis* and the Gram-negative bacterium *Escherichia coli* was performed.

2. Experimental

Usually, combustion-method involves exothermic redox reaction of suitable oxidizers and organic fuel to yield the oxide products. The stoichiometric compositions of the redox mixtures that are used for the combustion synthesis are calculated based on the total oxidizing (O) and reducing (F) valencies of the components. These coefficients are then used to calculate the stoichiometric balance so that the equivalence ratio (ratio of the oxidizing valency of the metal nitrates, O, to the reducing valency of the fuel, F) is unity. The unity value of the O/F ratio ensures that the released combustion energy i.e., used is the maximum [27].

Undoped and Cr-doped ZnO powders were prepared using a combustion method that involves a highly exothermic reaction between metal nitrates and an organic fuel that produces high temperatures for the crystallization of the product. As per the typical synthesis, the following precursors are employed: zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), urea ($\text{CH}_4\text{N}_2\text{O}$) and the dopant of chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). The starting materials were dissolved in a minimum quantity of deionized water and then heated at 90°C for 20 min in a glass beaker to obtain a homogeneous solution. This beaker was then transferred into a muffle furnace that had been preheated to $500 \pm 10^\circ\text{C}$, resulting in the initial boiling of the contents of the beaker along with the formation of foam. This stage was followed by the appearance of the combustion-gas flame, while the entire combustion process was completed within 5 min. The combustion product is foamy. The beaker was removed from the muffle furnace, and the product was crushed into a fine powder and then used for further characterization.

The XRD studies were conducted using the Philips X'pert X-ray diffractometer (Malvern PANalytical, The Netherlands) at a scan rate of 4°min^{-1} in the 2θ range of $10\text{--}90^\circ$ using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The FTIR spectrum was taken using the Perkin-Elmer RX1 instrument in the range of $400\text{--}4000 \text{ cm}^{-1}$. The morphology of the powders was obtained using the 4000EX SEM (JEOL, Japan). The PL measurements were carried out at room temperature (RT) using the RF-5301PC spectrofluorophotometer (Shimadzu, Japan) equipped with a xenon flash lamp.

The antibacterial susceptibility of the undoped and Cr-doped ZnO was tested using the disc-diffusion method. The bacterial strains that were used in this study are *B. subtilis* KCTC 1021 (Gram positive) and *E. coli* KCTC 1682 (Gram negative), which were obtained from the Korean Collection for Type Culture (KCTC; Daejeon, Korea). The strains were cultured in nutrient broth (NB) at 37°C for 18 h in a shaking incubator, and subsequently, the bacterial cells were adjusted to the turbidity of a 0.5 McFarland standard and spread onto an NB agar (Difco, USA) in a Petri dish [28,29]. The undoped and Cr-doped ZnO were diluted using sterilized water. The Advantec 6 mm disc (Toyo Roshi Kaisha, Japan) containing powder samples was spotted on the agar plates that were incubated at 37°C for 24 h. The zone of inhibition around the colonies was then measured along with the performance of antibacterial-susceptibility testing in at least triplicate for each strain.

3. Results and discussion

The XRD patterns of the undoped and Cr-doped ZnO powders are shown in figure 1a and b, respectively. All the diffraction patterns agree with the Joint Committee on Powder Diffraction Standards (JCPDS) file no. 80-0075 with regard to ZnO. The observed patterns of both samples exhibited similar diffraction patterns and can be indexed as the

Figure 1. Powder XRD patterns of (a) ZnO, (b) ZnO:Cr and (c) JCPDS no. 80-0075.

Figure 2. FTIR spectrum of ZnO at RT.

hexagonal structure of ZnO. The diffraction patterns clearly show that the introduction of a small amount of the Cr ion exerts almost no effect on the basic crystal structure of ZnO. The crystallite size D can be estimated from the broadened peaks using the following Debye–Scherrer equation: $D = 0.9\lambda/\beta \cos \theta$, where β is the full width at half maximum of the diffraction line that is located at the angle θ and λ is the XRD wavelength. The strongest peaks were used to calculate the sizes. The estimated crystallite size of both samples is $\sim 31.18 \text{ nm}$. It is significant that the pure-ZnO phase can be achieved using a simple and fast combustion method at low furnace temperatures.

The FTIR spectrum of the combustion-synthesized ZnO in the range of $400\text{--}4000 \text{ cm}^{-1}$ is shown in figure 2. The broad band between 3200 and 3600 cm^{-1} is due to the vibration mode of the chemically bonded hydroxyl groups [28]. The band at $\sim 1622 \text{ cm}^{-1}$ is due to the deformation vibrations of

Figure 3. SEM images of ZnO at low and high magnifications.

weak-bound water. The two strong and sharp bands at 539 and 440 cm^{-1} are attributed to the stretching modes of ZnO, and they indicate high crystallinity of the prepared powders. Mostly, similar results were observed for the Cr-doped ZnO-powder sample (figure not shown).

To determine the surface morphology of the sample, SEM investigations were carried out. Figure 3 shows the representative SEM micrographs that were taken for ZnO. The SEM micrograph at a low magnification as shown in figure 3A shows a porous network due to the rapid release of gases during combustion. This porous network can be clearly observed in figure 3B, which is a magnified view of zone (a) of figure 3A. Figure 3B shows the ZnO particles that are interconnected to make a large network system with irregular pore sizes and shapes; this type of interconnected porosity is a unique feature of this combustion method. The irregular sizes and shapes are attributed to the nonuniform distribution of the temperature and the mass flow during combustion. This feature type regarding ZnO particles is inherent to the combustion process.

The PL spectrum of the combustion-synthesized ZnO is shown in figure 4. Figure 4a shows the excitation spectrum of the prepared ZnO, where the excitation band ($\lambda_{\text{emi}} = 383 \text{ nm}$) shows a maximum at 268 nm. Figure 4b shows the emission spectrum of ZnO, where the emission band ($\lambda_{\text{exi}} = 268 \text{ nm}$) shows a maximum at 383 nm; this emission band is the result of the recombination of the free excitons through an exciton–exciton collision process. In the literature, the violet emission at around 383 nm was considered as a near-band-edge emission [29]. Wahab *et al* [30] studied the PL properties of ZnO nanoparticles that had been prepared via a nonhydrolytic-solution route, and they observed the emission band at 382 nm when a 325 nm helium–cadmium laser line served as the excitation source. These observations revealed that the PL-emission intensity of Cr-doped ZnO is quite poor compared with that of pure ZnO (figure not shown). Lu *et al* [31] observed that the PL-emission intensity of silver (Ag)/ZnO nanocomposites is lower than that of pure ZnO. They reported that the Ag

Figure 4. PL spectrum of ZnO. (a) Excitation spectrum ($\lambda_{\text{emi}} = 383 \text{ nm}$) and (b) emission spectrum ($\lambda_{\text{exi}} = 268 \text{ nm}$).

nanoparticles acted as electron sinks, thereby hindering the recombination of the photoinduced electrons and holes, and this accounted for the reduced PL-emission intensity [32].

The antibacterial activities of the undoped and Cr-doped ZnO powders were tested using the Gram-positive bacterium, *B. subtilis*, and the Gram-negative bacterium, *E. coli*. Figure 5 shows the images of the bacteriological tests of *B. subtilis* and *E. coli* on the agar plates without the doped ZnO powder and with the Cr-doped ZnO powder. Antibacterial activity was not observed in the undoped ZnO samples for both the Gram-positive bacterium, *B. subtilis*, as shown in figure 5A, and the Gram-negative bacterium, *E. coli*, as shown in figure 5B. The Cr-doped ZnO, however, showed antibacterial activity against the Gram-positive bacteria, *B. subtilis*, as can be seen in figure 5C. Similar to the undoped sample, the Cr-doped ZnO sample showed almost no antibacterial activity for the Gram-negative bacterium, *E. coli*, as shown in figure 5D. It is known that the cell wall material in Gram-negative bacteria differs

Figure 5. Disc-diffusion assay. Inhibition zone against the growth of: (A) *B. subtilis* with ZnO, (B) *E. coli* with ZnO, (C) *B. subtilis* with Cr-doped ZnO and (D) *E. coli* with Cr-doped ZnO.

much in their properties when compared with Gram-positive bacteria. This includes the thickness of peptidoglycan, the presence of periplasmic space, higher content of lipid and lipoproteins in the cell wall of the Gram-negative species, which makes it highly resistant to an external antibacterial agent. In this study, the nanoparticle treatment not showed any cell damage or cell wall disruption in *E. coli* (Gram-negative bacterium) and representing no antibacterial activity which leads to no inhibition or suppression of the bacterial growth. The observed antibacterial activity increased with the increased concentration of the Cr-doped ZnO powder, as shown in figure 5C. The antibacterial activity at the high concentration of the Cr-doped ZnO powder (200 mg l⁻¹) is 1.5 times higher than that of the low-concentration sample (25 mg l⁻¹). In comparison, the undoped ZnO sample showed

almost no bactericidal activity compared with the Cr-doped ZnO powder. The results are summarized in table 1.

According to previous reports [33,34], the exact antibacterial-susceptibility mechanism of the undoped and metal-ion-doped ZnO is still unclear, and it may involve in the generation of reactive oxygen species (ROS), the release of Zn²⁺ ions and the damage of the cell membranes. In the literature [35], several possible mechanisms including the penetration of the cell envelope and the disorganization of the bacterial membrane [36], Zn²⁺ binding to the microorganism membranes [37] and the photocatalytically generated ROS on the oxide surface [38] have been suggested. It was found that upon doping a small amount of transition metal into host matrices increases the surface defects leading to higher biological activities and also affects the optical and electronic

Table 1. Antibacterial activity caused by undoped-ZnO and Cr-doped-ZnO powders through the implementation of the agar-diffusion method.

Powder	Conc. (mg ml ⁻¹)	Antibacterial activity	
		<i>Bacillus subtilis</i>	<i>Escherichia coli</i>
ZnO	0	—	—
	25	—	—
	50	—	—
	100	—	—
	200	—	—
Cr-doped ZnO	0	—	—
	25	+	—
	50	+	—
	100	+	—
	200	+	—

— Denotes the absence of susceptibility and + denotes the presence of susceptibility.

properties. In particular, transition metal Cr is quite interesting, because it modifies the surface properties of metal oxide nanoparticles and therefore increases its disposable and saturation kinetics with living cells. An earlier study has shown the importance of Cr doping in metal oxide nanoparticles in the antibacterial activity [39]. In the present study, though Cr-doped ZnO showed the synergetic effect on the antibacterial activity, however, the reports on chromium oxide alone showed independent antibacterial action in different bacterial strains [40,41]. It seems that the explanation of a detailed mechanism of the activities of the undoped and metal-ion-doped ZnO is still under debate.

4. Conclusion

The potential of the urea–nitrate combustion synthesis is outstanding in terms of its highly pure and crystalline ZnO yield. The advantages of this synthesis include process simplicity, rapid reaction completion and low processing temperature; therefore, this method can replace the conventional powder methods. XRD analysis enables the conclusion that the phase of the prepared ZnO material is hexagonal. The FTIR results show an intense broad band in the vicinity of 400–600 cm⁻¹ that indicates ZnO vibration. The SEM micrographs show an interconnected porosity that is an attribute to the synthesis method. The PL studies on the sample showed that the existence of a near-band-edge emission at ~383 nm indicates that the crystalline nature of the prepared ZnO material is well established with no structural defects. The results of the antibacterial testing demonstrated that the Cr-doped ZnO sample shows a viable reduction of the *aureus* strains of the Gram-positive bacterium, *B. subtilis*. Further, although this finding is preliminary in nature, the present results suggest that Cr-doped ZnO may serve as a promising material in biomedical applications due to its antibacterial activity.

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